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TIME-RESOLVED MAGNETIC DISPERSION MASS SPECTROMETRY:

A TECHNIQUE FOR MULTIDIMENSIONAL ANALYSIS

by

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are given, various scanning modes are described, and the expected
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The potential for the technique in analytical applications is con-
sidered, particularly in light of a proposed high-speed data
acquisition system.

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Brief

A new mass spectral technique that provides energy-independent parent and daughter mass assignment is proposed. All conventional MS/MS data, including parent, daughter, and neutral loss scans can be obtained.

Abstract

A new type of multidimensional mass spectrometer is presented. Utilization of ion beam pulsing and time-resolved detection techniques in a magnetic sector mass spectrometer allows simultaneous momentum and velocity analysis of the ions. This combination of factors provides parent ion and daughter ion mass assignments that are independent of ion energy. Parent, daughter, and neutral loss spectra can be obtained as in current MS/MS instruments. Equations for mass determination are given, various scanning modes are described, and the expected resolution and sensitivity are evaluated. Demonstration data are presented for daughter ions of a selected metastable decomposition. The potential for the technique in analytical applications is considered, particularly in light of a proposed high-speed data acquisition system.

The ability to identify parent-daughter ion relationships that result from metastable ion decomposition or from collision-induced dissociation (CID) has become increasingly important in recent years. Spectra showing all the daughters of a specific parent ion (daughter spectra) are proving invaluable for many applications in mixture analysis and structure elucidation (1-3). So also are spectra which show all the parents of a particular daughter mass (parent spectra) or spectra of ions that undergo a particular neutral loss (neutral loss spectra). These types of spectra are normally obtained with various tandem (sequential) arrangements of mass-selective devices referred to as MS/MS instruments.

Two types of MS/MS instruments are commonly in use and are commercially available: tandem sector instruments of which the mass-analyzed ion kinetic energy spectrometer (MIKES) (4) is an example, and tandem quadrupole instruments such as the triple quadrupole mass spectrometer (TQMS) (5). Both types of instruments operate in a sequential manner: (a) parent ion selection, (b) parent ion dissociation, and (c) daughter ion selection. The sequential nature of these operations, however, allows examination of only one combination of parent and daughter ion masses at a time. The collection of the complete MS/MS data field (all the daughters of all the parents) can require tens of seconds to several minutes. Thus full MS/MS analysis is available only for samples that can be continuously introduced into the source over a relatively long time.

A potentially much faster method for generation of the multidimensional MS/MS data is through simultaneous momentum and velocity measurements. Such measurements can be made with a single sector mass spectrometer modified for ion

source pulsing and time-resolved detection. The magnetic sector provides analysis of ion momentum while the combination of a pulsed ion source and time-resolved detection system provides analysis of the ion velocity through the instrument. Figure 1 illustrates the basic components of a single sector mass spectrometer and shows the separation of ions based on velocity and momentum. Approximately monoenergetic ions extracted in a brief pulse from the source may undergo fragmentation in the field-free region preceding the magnet. The magnetic field disperses the ions according to their momenta, daughter ions now having less momentum than their parents. At the same time, ions become separated along the ion path as a result of their different velocities. However, the velocity of a daughter ion remains essentially the same as that of its parent ion, altered only slightly by the dissociation process, so all daughter ions of the same parent will have nearly identical velocities. For a single value of the magnetic field, the ion packet corresponding to stable ions with the selected momentum will arrive at the detector, followed in time by daughter ions with the same momentum which originated from fragmentations of progressively heavier (and slower) parents. If a current-time curve is taken for each value of magnetic field strength (momentum), the complete set of MS/MS spectra for the sample can be obtained from the resulting data set. As will be shown, the mass assignment for any ion (daughter or stable ion) is based solely on the combination of its field strength and arrival time, and is completely independent of its energy. Daughter ion, parent ion, and neutral loss spectra can be constructed from the complete data set or can be obtained by various independent and linked scans of the magnetic field strength and ion arrival time.

Time-resolved detection of magnetically dispersed ions can be accomplished with instrumentation that is simpler and more commonly available than tandem MS/MS instrumentation, and could provide the complete MS/MS data field at a dramatically greater rate. The feasibility and potential capabilities of this new type of mass spectrometer, along with confirming data from a simple test system, are examined in this paper.

Mass Assignment for Parents and Daughters

For a mass spectrometer in which the ions are accelerated out of the source with the same kinetic energy, the velocity of the ions is given by Equation 1,

$$\frac{1}{2} m v^2 = z e V \qquad (1)$$

where m is the ion mass, v is the velocity, z is the number of charges on the ion, e is the electronic charge, and V is the accelerating voltage. Either by pulsing the accelerating voltage or deflecting the ion beam, a pulse of nearly mono-energetic ions can be produced. After acceleration, the velocity of any ion is inversely proportional to the square root of its mass. As the accelerated ions travel through space, they separate according to mass, the lightest ions travelling fastest. The time-of-flight, t, of ions reaching a detector of fixed distance, ℓ, from the pulsing device is given by Equation 2.

$$t = \frac{\ell}{v} \qquad (2)$$

Equations 1 and 2 can be combined to give Equation 3 - an expression relating

$$\frac{m}{z} = \frac{2 \ V \ e \ t^2}{\ell^2} \qquad (3)$$

the mass-to-charge ratio of an ion to its flight time. This is the equation for mass determination in a time-of-flight mass spectrometer.

Ions travelling at right angles to a uniform magnetic field are dispersed along various arcs according to their momenta, as given by Equation 4, where $\underline{B}$

$$m \ v = B \ z \ e \ r \qquad (4)$$

is the magnetic field strength and $\underline{r}$ is the radius of the ion's circular path. Simultaneous measurement of the flight time of an ion (inversely proportional to velocity) and the magnetic field at which that ion passes the detector entrance slit (proportional to momentum) provides the necessary data for determination of the ion mass. This is expressed in Equation 5 which can be derived by combining

$$\frac{m}{z} = B \ t \left(\frac{e \ r}{\ell} \right) \qquad (5)$$

Equations 2 and 4. Thus, the combination of a momentum analyzer and a velocity analyzer effectively produces a mass-to-charge ratio determination that is independent of ion energy. An important consequence of this energy-independent mass determination is the ability to accurately assign the mass, even for a single ion. Accurate energy-independent assignment of mass holds not only for stable ions but also for ions which change mass in the field-free region between the ion acceleration region and the magnetic sector. This fact can be exploited to perform experiments normally done with a tandem mass spectrometer.

The daughter ion arising from either unimolecular decay or collision-induced dissociation, which occurs in the field-free region preceding the magnet, will be transmitted to the detector. When the field strength corresponds to its true momentum, the combination of magnetic field strength and arrival time can be used to make an accurate mass assignment according to Equation 5. Thus masses of all ions, parents and daughters, will be determined accurately by the combination of momentum and velocity. The velocity of a daughter ion will be nearly the same as that of its precursor (parent) ion since the release of kinetic energy in the fragmentation process alters the velocity only slightly. Hence, the use of the measured flight time of the daughter ion in Equation 3 can be used to identify the mass of the parent from which the daughter originated. The possible spread in daughter ion velocities through fragmentation might, however, make it more difficult to tell which of the stable ions in a closely packed cluster are their parents. All ion mass determinations therefore involve a combination of the momentum selection techniques used in magnetic sector mass spectrometry and the ion flight time measurement techniques used in time-of-flight mass spectrometry. These latter techniques are reviewed in the next section.

Time-Resolved Detection Techniques

Spectral Acquisition by Time-Slice Detection. In conventional time-of-flight mass spectrometry, recorded spectra, either on paper or in digital form, are normally obtained with a gated detection scheme in which ions of only one arrival time are detected in a narrow time slice or aperture that is triggered at a specified delay after the ion pulse is initiated. (This can be called time-slice detection or TSD.) The aperture delay then is increased

slightly for each successive pulse of the source to cover all arrival times. This process usually takes 1-10 seconds.

To appreciate how this technique can be used to obtain the spectra available with current MS/MS instrumentation, consider Figure 2, a plot of magnetic field strength versus ion flight time showing the loci of peaks for several types of scans, i.e., each line marks the possible values of B and t along which peaks might be observed for the indicated scan. Ion int , y, while not explicitly shown, would be represented as peaks "out of the ie". For example, if the arrival time that is sampled by time slice detectior ~D) is held constant at the arrival time of a parent ion, only parent ion , its daughters will be detected when the magnetic field is scanned. The result is a daughter ion scan, which is shown for parent mass 400U.

A parent ion scan produces a spectrum of all parents that fragment to produce a particular daughter ion. This is achieved by scanning the sampled time slice along with the magnetic field strength so that the product Bt is kept constant. In this "linked" scan of constant Bt, ions of the same mass will be measured, the arrival times revealing the masses of the parents that produced the selected daughter mass.

One additional type of scan, often useful for the screening of mixtures, is the neutral loss scan. This is a scan of all the parents that fragment to lose a particular neutral mass. The neutral mass that is lost in the fragmentation process $m_3 = m_1 - m_2$, can be held constant by a more complex "linked" scan, as given by Equation 6, the difference of Equations 3 and 5. A plot of B vs. t

$$m_3 = \frac{2\,V\,e\,t^2}{\ell^2} - \frac{B\,r\,e\,t}{\ell} \tag{6}$$

illustrating this linked scan is shown in Figure 3. Analogous to Figure 2, this plot shows several lines, each marking all possible values of $\underline{B}$ and $\underline{t}$ for the stable ion or neutral loss scan indicated.

Mass assignment for an ion that does not decompose after leaving the source, i.e., a stable ion, should be the same whether calculated from Equation 3 or Equation 5 (though the determination from Equation 5 is unaffected by ion energy). Equations 3 and 5 can be combined to give Equation 7 which is only

$$t_s = \frac{B\,r\,\ell}{2V} \tag{7}$$

valid for stable ions. This equation indicates the *flight time at which stable* ions can be observed for a given value of the magnetic field and is represented as the diagonal line in Figures 2 and 3. Thus, by limiting the observation to this time function, $\underline{t}_s$, stable ions can be determined while screening out any ions that result from metastable or CAD fragmentation processes. Conversely, by observing all ions for which the arrival times are longer than $\underline{t}_s$ while scanning $\underline{B}$, a spectrum of daughter ions without any stable ions would be obtained. Such a "metastable spectrum" might be useful as a "fingerprint" for a compound.

Spectral Acquisition by Time-Array Detection. One of the advantages of the conventional time-of-flight mass spectrometer is the opportunity to detect all the ions in each pulse of the ion source, not just those of a particular mass. In the past, this was possible only with an oscilloscope which, of course, does

not retain the information for later processing. As a result, time-slice detection has been the predominant method for obtaining TOF spectra. However, in using TSD, ions of all arrival times other than those observed in the specified time-slice are ignored. The result is equivalent to scanning a mass filter, i.e., while ions of one mass are being measured, ions of all other masses are discarded. It has been recently demonstrated that whole sections of a time-of-flight spectrum can be acquired digitally during a single ion pulse (6-8). Though offering improvements, the transient recorders and similar devices used for these studies utilize only a fraction of the mass range and repetition rate capabilities of time-of-flight instruments. A vast improvement in scan speed, sensitivity, and dynamic range could be realized if arrival times of all ions in each pulse were acquired at the maximum pulse rate. (This can be called time-array detection or TAD). For typical values of the accelerating voltage (3.5kV) and analyzer tube length (1.0m), all ions from one pulse of the source (1-1000U) will arrive at the detector in less than 40 μs. Thus, repetition of the ion pulses at a rate of up to 25kHz will require a detector system with very rapid data throughput. This would be possible with an integrating transient recorder of advanced design. An instrument such as this is presently being developed in our laboratory (9).

The repeated sequence of scans necessary to obtain spectra by TSD can be eliminated with TAD. Time-array detection will make possible, in a single scan of the magnet, the detection of ions for all values of B and t, i.e., all the daughters of all the parents. The result will be a data matrix from which the gamut of MS/MS spectra can be retrieved. Similar data matrices have been obtained in the "B-E plane" of a double-focusing mass spectrometer, although in

these cases multiple scans were necessary to acquire all the data (10). The ability to extract any desired scan f >m the data matrix by post-analysis processing frees the analyst from the need to decide ahead of time which scans would be most useful for a particular sample. The full data matrix would be obtained with TAD in the same time required by any of the single scans with TSD.

The consequence of rapid acquisition of the data matrix will be to open up new opportunities for the full use of MS/MS. The use of a tandem mass spectrometer as a very selective and informative detector for gas and liquid chromatography has in the past been restricted to selected reaction monitoring and very limited scanning of parent or daughter ions. A more rapid acquisition of MS/MS data can make GC-MS/MS and LC-MS/MS much more powerful analytical techniques. Other applications of MS/MS not utilizing on-line chromatographic separation, such as structure elucidation and studies of fragmentation pathways, could be carried out significantly more rapidly and consequently with much less sample.

Expected Performance Characteristics

Mass Resolution of Stable Ions and Daughter Ions. The mass resolution can be evaluated by considering the contributions to the uncertainties in the Bt product by the experimentally-measurable quantities. The precision in the magnetic field measurement is determined by the field inhomogeneity, field stability, the effect of fringing fields, as well as the precision of the signal from the magnetic field sensor and the accuracy of the calibration procedure. The uncertainty in path radius is determined by the slit widths. The resulting

mass uncertainty due to the magnetic sector should be the same as that obtained with the magnetic spectrometer operated in normal (non time-resolved) mode with monoenergetic ions. Timing precision is limited by the uncertainty in the start time, the accuracy in measuring the delay time, and the aperture window of the sampling electronics. Precision in the flight length is determined by the depth of the ion volume sampled and by the different paths through the magnetic sector due to first-order focusing in the sector. Flight time precisions comparable to those achievable with modern time-of-flight mass spectrometers when measuring monoenergetic ions should be achievable.

Figure 4 is an expanded portion of a hypothetical $B-t$ plane for stable ions of similar mass. The solid curves represent the signal expected when the uncertainty in the radius and path length is zero. The shaded regions containing the solid curves represent the "width" of each curve determined by uncertainties in the radius and path length. The uncertainties in B and t are also shown. Energy differences in ions of the same mass will cause them to spread out along the lines of constant Bt as shown by the length of the line, but will cause no increase in the width of the line. Higher energy ions will appear at shorter arrival times and higher field strengths. Similarly, lower energy ions will appear at longer arrival times and lower fields. Resolution in two dimensions removes the effect of energy spread on mass determination, hence, the time-resolved magnetic dispersion mass spectrometer should provide unit mass resolution of both stable and daughter ion masses. Conversely, measurement of the distribution of ions along this line will provide an energy spread profile useful for studying the energetics of ion formation or fragmentation (11).

"Energy focusing", normally required in time-of-flight analysis to improve the resolution (12,13), is not needed. "Space focusing" to correct for variations in the point of ion formation in the source can be optimized without the need to worry about its incompatability with energy focusing (14). In some ways the magnet acts as an energy filter for TOF analysis. Indeed, magnets have been previously used with TOF to filter out ions with large energy deviations, such as those produced in laser desorption (15,16). Magnets have also been proposed for focusing ions with equal momentum acceleration (17). Thus, magnetic dispersion could provide an alternative to other methods of dealing with energy spreads, such as the "Mamyrin reflectron" (18).

Figure 4 can also be used to compare the expected resolutions for simple magnetic, simple time-of-flight, and time-resolved magnetic dispersion mass spectrometers. In the magnetic instrument with no time resolution, the ion intensity would be projected onto the B axis only. The right end of the higher mass peak will overlap with the left end of the lower mass peak to give less than fully resolved peaks. Likewise, in a TOF instrument, the two peaks will overlap on the time axis giving less than complete resolution. On the other hand, the time-resolved mass spectrometer determines a two-dimensional section of the plot and as such is potentially capable of a higher resolving power. The masses represented by the two curves will be completely resolved if the region delineated by δB and δt contains relatively little ion intensity in the Bt space between curves. Resolution becomes limited at high masses where the separation of Bt curves for masses separated by 1U becomes small.

Effect of Kinetic Energy Release during Fragmentation. Due to the release
of kinetic energy during the dissociation process (typically less than 1eV), the
daughter ion velocity is usually not exactly the same as its precursor, although
the difference is generally very small (19). Two factors affect the velocity
difference and are manifested in terms of spreading on the B vs. t plane of
Figures 2 or 4. The first is a spread in ion intensity along a curve of
constant Bt which is caused by the actual spread in ion velocities before or
after fragmentation. The second effect results from the difference between a
daughter ion's velocity and that of its precursor, so that the measured flight
time does not give the true velocity of the daughter, but a function of the
velocities before and after dissociation. When a large acceleration energy is
used, the velocity differences are small, and they will manifest themselves as a
slight broadening, not of the peaks, but a widening of the Bt curve itself,
since the value of t does not correspond to the true velocity of the ion whose
momentum was selected. The error in the measured velocity resulting from a
velocity change can be minimized by making the distance of travel after the
collision chamber much larger than the distance before, i.e., by placing the
collision cell as close to the ion source as possible. A distance ratio of 500
or more is practical and for a 1% velocity change (greater than would be
experienced) the error would be only 0.002%.

In moving along a curve of constant Bt, daughter ion peaks would generally
show a larger energy spread than stable ion peaks. For a large kinetic energy
release, daughter ions might vary enough from the velocities of their true
parent to overlap the velocities of parents close in mass to the true parent.
Correct assignment of the parent ion mass in this case could be aided by peak

intensity centroiding along the Bt curve. For more serious cases involving daughter ion arrival time overlap, factor analysis or other chemometric techniques could be invoked.

Dissociations within Non-Field-Free Regions. Mention should also be made of one additional factor that will affect the appearance of the spectrum and the resolution. Ions that dissociate during acceleration or within the magnetic sector itself can contribute to low signal levels throughout the spectrum, though usually these effects are negligible. Dissociations within the accelerating field do not affect the daughter ion mass assignment because this mass assignment is solely defined by the value of Bt. The arrival time will decrease, though, resulting in a low-level continuum along the curve of constant Bt between the arrival time for a stable ion and the arrival time for the same transition occuring in the field-free region. Likewise, dissociations within the magnetic sector result in a continuum that extends from the stable ion Bt position to the daughter ion Bt position along a line of constant arrival time.

Sensitivity. The expected sensitivity of the time-resolved magnetic dispersion mass spectrometer can be estimated by comparison with a conventional magnetic sector mass spectrometer. Relative to the conventional instrument, sensitivity will be limited a) by the low duty cycle of the ion beam pulsing (the time the beam is "on" relative to the total time of the pulsing cycle) and b) by the increased resolution in both time and magnetic field strength necessary when precise mass values are required.

The loss of ion intensity due to the pulsing requirements depends on the mechanism used to create the pulse. Continuous ionization and ion extraction followed by beam deflection (20,21) discards all ions which are not within the sampled segment of the ion beam. Signal strength in this case would be related to the duty cycle. For example, if time resolution requirements necessitate approximately a 10ns wide ion packet, with a cycle duration of 25µs, only 10ns/25µs (0.0004) of the ions extracted would be utilized. In other words, this technique would provide a sensitivity of 0.0004 times that of the same magnetic instrument without velocity analysis.

The beam deflection technique represents the worst case. A more favorable source pulsing mechanism would be the one used in conventional time-of-flight instruments. Ions are generated for a period of time between pulses after which a voltage pulse is applied to an extraction grid to form the ion packet. Some of the ions formed between pulses are held in the source by the space charge of the electron beam until the extraction takes place. For example, holding and extracting only 4% of the ions produced between pulses would result in 100 times more ion charge in the packet than the beam deflection technique would give. Other methods of efficient ion generation or ion storage prior to extraction may also prove useful. For example, when pulsed desorption/ionization from a sample surface is used, virtually no sample need be lost between pulses.

The addition of time resolution to the momentum resolution of the sector instrument can result in a loss in sensitivity in much the same way as the addition of an electric sector to form a double-focusing instrument. As the previous discussion of resolution demonstrated, precision in the mass assignment

is limited by the precision in the measurement of the arrival time. Obviously, decreasing the arrival time aperture would lead to a concomitant loss in sensitivity at any one time slice. As with other types of resolving instrumentation, sensitivity and resolution are reciprocally related and trade-offs are made based upon specific analysis requirements.

Effect of Time-Resolving Technique on Sensitivity. With time-slice detection (TSD) the time-resolved magnetic dispersion mass spectrometer acts as a dual filter device; ions of only a single momentum are selected by the magnet and slits, and ions of only a single velocity are selected by the gated detector. At any one point in the analysis the vast majority of ions being pulsed out of the source are discarded which results in the same inefficient use of ions that occurs in tandem MS/MS instruments. However, for many analyses ions of all momenta and velocities are not needed. If a daughter ion scan of only one parent ion is desired, for example, only one arrival time is required. (Additionally, in this type of scan the time window can be enlarged to improve sensitivity, even to the point where little signal is lost due to the time resolution. The time window need only be small enough to exclude ion intensity from ions of adjacent arrival times). On the other hand if daughter ion scans of all possible parent ions are needed, time-slice detection necessitates multiple scans of either the magnetic field or arrival time.

In time-array detection (TAD) arrival times of all ions in each pulse of the source are measured. In this way the instrument acts like a filter followed by an analyzer that resolves without loss of information since all ions of the selected momentum are measured and stored. There are several advantages to this

approach. When high resolution in the arrival time is desired, sensitivity may be lower for any given measurement coordinate, however, the total signal will still be acquired throughout all measurement coordinates and the sensitivity can be retrieved during post-experiment processing. Secondly, since ions of all velocities are monitored at each magnetic field strength, all the possible tandem mass spectral information can be obtained in a single scan of the magnet. In order to recover the sensitivity lost due to the duty cycle factor, multiple scans of the magnet could be averaged. There is a choice; all MS/MS information could be obtained in a small fraction of the time required for the same acquisition by MIKES or TQMS but with lower sensitivity, or the complete set of MS/MS spectra could be obtained in the same time as required by MIKES or TQMS but effectively with higher sensitivity.

Experimental

Pulsing by Ion Beam Deflection. Experiments were performed on an LKB-9000 mass spectrometer. The instrument was not altered physically and was operated in the normal manner with the exceptions noted below. The ion beam deflection plates, normally used for focusing and located immediately after the entrance slit, were used to sweep the ion beam across the magnetic sector entrance and thus produce a packet of ions (20,21). Each deflection plate was connected to a separate high voltage dc power supply. After adjusting the voltage on each plate to give maximum ion beam focus, a 50V peak-to-peak square wave signal was super-imposed on the voltage of one of the plates to deflect the ion beam. The beam was deflected away from the exit slit during the HI and LO levels of the square wave so that only during the rising and falling edges of the square wave

was the beam focused on the exit slit. The rising and falling edges of the square wave signal were also used to trigger the oscilloscope sweep.

The output of the electron multiplier was amplified and displayed on an oscilloscope screen. Arrival times were measured relative to the square wave transition by analysis of photographs of the screen displaying multiple repetitive traces.

Samples used were reagent grade and were introduced via the heated gas inlet. Instrument pressure was maintained at 1×10^{-6} torr. The trap current was set at $60 \mu A$ and the accelerating voltage was 3555V.

Results

Measurements were made on compounds known to have strong metastable decompositions. The results for the metastable loss of HCN from the molecular ion of benzonitrile are shown in Figure' 5. At the magnetic field strength corresponding to stable ions of mass 103 the arrival time was 14.1 μs. At the magnetic field strength corresponding to stable ions of mass 56, a peak at 10.6 μs was observed for the stable ions. A second peak was also seen at this field strength with an arrival time of 14.1 μs. Calculation of the product Bt indicates that second peak consisted of ions of mass 76 and the arrival time indicates these ions are daughters of a parent of mass 103. Note that mass 56 is the apparent mass calculated for the metastable peak observed. That is, the daughter ions of mass 76 and stable ions of mass 56 have the same momentum.

The peaks shown in Figure 5 are reproductions of the oscilloscopic display. These data demonstrate the validity of the technique and verify the equations but they do not represent the optimum in performance. Much improved resolution should be obtained through continuing refinements of the instrument, especially with the addition of high-speed detector electronics.

Other Applications of Time-Resolution

Alternate modes of operation of the time-resolved magnetic dispersion mass spectrometer. The magnetic field and ion flight time are only two of the three parameters that can be experimentally changed in seeking MS/MS information. According to Equations 3 and 5, the accelerating voltage can also be varied. For example, if a constant magnetic field were used, the daughter ion mass would be linearly proportional to the arrival time and the parent ion mass would be obtained from the product Vt^2 . A parent ion scan (constant daughter) could be obtained with TSD by setting t to give a constant value of Bt and scanning V to select different parent ions. However, there are several disadvantages found in scanning the accelerating voltage. These include, a) loss of sensitivity resulting from defocusing the ion source (22), b) changes in detector response with different ion energies (23), c) changes in collision cross-sections with different energies (24), and d) changes in the relative contribution of thermal energy to the total ion energy.

Ions can also be accelerated to constant momentum, rather than constant energy, by terminating the extraction voltage pulse before any ions can traverse the full field (25). This has the advantage of producing a time-of-flight axis that is linearly related to the parent ion mass. However, constant energy

acceleration generally provides better resolution (26) which makes it the preferred mode of operation.

Implementation of Time-Resolution with other Devices. The concept of time-resolved detection can be employed with other mass spectrometers as well as the magnetic sector mass spectrometer. For example, the electric sector, most often used in double-focusing mass spectrometers and in ion kinetic energy spectrometers, is amenable to time-resolved detection. The electric sector is an energy filter that obeys equation 8, where E is the electric field at radius

$$\frac{m\,v^2}{r} = z\,e\,E \tag{8}$$

r. Ions are accelerated to constant energy in the source and normally the electric field is adjusted to pass ions of that energy. Excepting any post-acceleration decomposition, time-resolved detection of the ions would be equivalent to time-of-flight analysis with increased resolution due to energy filtering, with the ion mass being given by equation 3. Were an ion to decompose in the field-free region between the entrance slit and the electric sector, measurement of the ion velocity by its time-of-flight, equation 2 will yield the parent ion mass as previously shown, independent of the ion momentum. Measurement of both ion velocity and electric field strength will yield the daughter ion mass, equation 9. Equation 9 follows from equation 8 by replacing

$$\frac{m}{z} = \frac{e\,r\,E\,t^2}{\ell^2} \tag{9}$$

the velocity with the flight time. Figure 6, analogous to figure 2, shows the relationship of electric field and arrival time for different types of ions in

the time-resolved ion kinetic energy spectrometer.

Various combinations of mass dispersive fields, such as found in double-focusing instruments, could also utilize time-resolved detection. For a normal geometry double-focusing mass spectrometer, decompositions in the first field-free region would then be energy filtered before time-resolved magnetic dispersion mass spectrometry. Decomposition in the second field-free region would give energy filtered parent ions prior to decomposition. The magnetic sector would momentum select the parents and the daughters produced in the second field-free region. For a reversed geometry instrument, decompositions in the first field-free region would be momentum filtered prior to time-resolved ion kinetic energy spectrometry. Decomposition in the second field-free region would allow the operator to select parent ions both by momentum and time-of-flight thus eliminating the possible ambiguity in parent ion mass assignment. If decompositions occur in both field-free regions, daughter ions formed in the first field-free region can undergo subsequent fragmentation to form granddaughter ions, both of which can be measured for an additional dimension of information.

Potential for Time-Resolved Magnetic Dispersion. The time-resolved magnetic dispersion mass spectrometer has the potential to make a significant contribution to mass spectrometry. Existing single sector mass spectrometers could be modified for time-resolved detection, thus inexpensively extending the capabilities for tandem mass spectrometry to many laboratories already equipped with magnetic sector spectrometers. Time-resolved magnetic dispersion mass spectrometry is complementary to existing tandem MS/MS techniques. It provides

good resolution of daughter masses as in tandem quadrupole instruments but utilizes the high energy collision-induced dissociation process of MIKES.

The addition of an integrating transient recorder to this instrument would increase the data throughput significantly. Once sufficient sensitivity is realized, the capabilities for performing GC-MS/MS or LC-MS/MS (to obtain all available MS/MS data on each chromatographic peak) could significantly advance the state-of-the-art for rapid, selective, and informative analyses.

Acknowledgements

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Credit

Captions

Figure 1 Ion separation by momentum and velocity in a time-resolved magnetic dispersion mass spectrometer. Daughter ions from the same parent mass appear at the same arrival time but are dispersed according to their momenta. Stable ions have shorter arrival times than daughter ions of the same momentum because of their greater initial velocity.

Figure 2 MS/MS data field ($\underline{B}$ $\underline{vs.}$ $\underline{t}$). Each line represents the locus of peaks for different types of ions ($\underline{V}$=3500V, $\underline{\ell}$ =1.0m, $\underline{r}$=0.2m). All coordinates below the stable ion line represent daughter ions. The points show the location of peaks for (a) stable ions of mass 400, (b) stable ions of mass 150, (c) daughter ions of mass 150 with parent of mass 400.
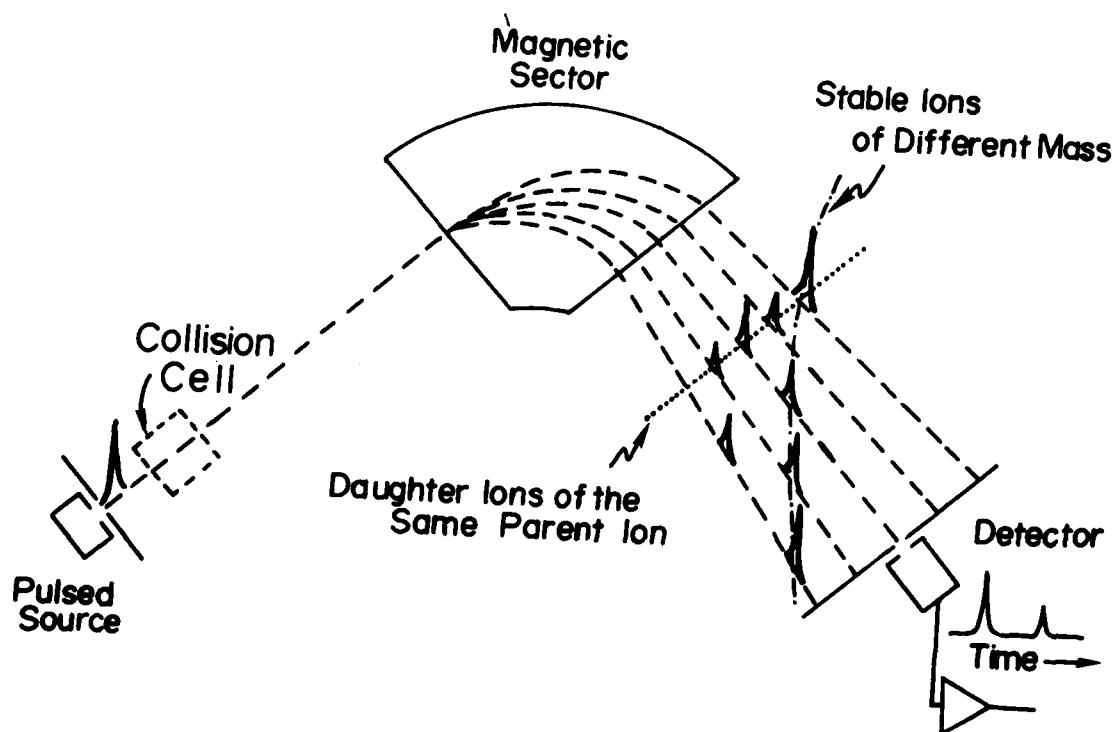
Figure 3 MS/MS data field showing the locus of peaks for stable ions and daughter ions resulting from several representative neutral losses, $\underline{m}_{\underline{3}}$. ($\underline{V}$=3500V, $\underline{\ell}$=1.0m, $\underline{r}$=0.2m).
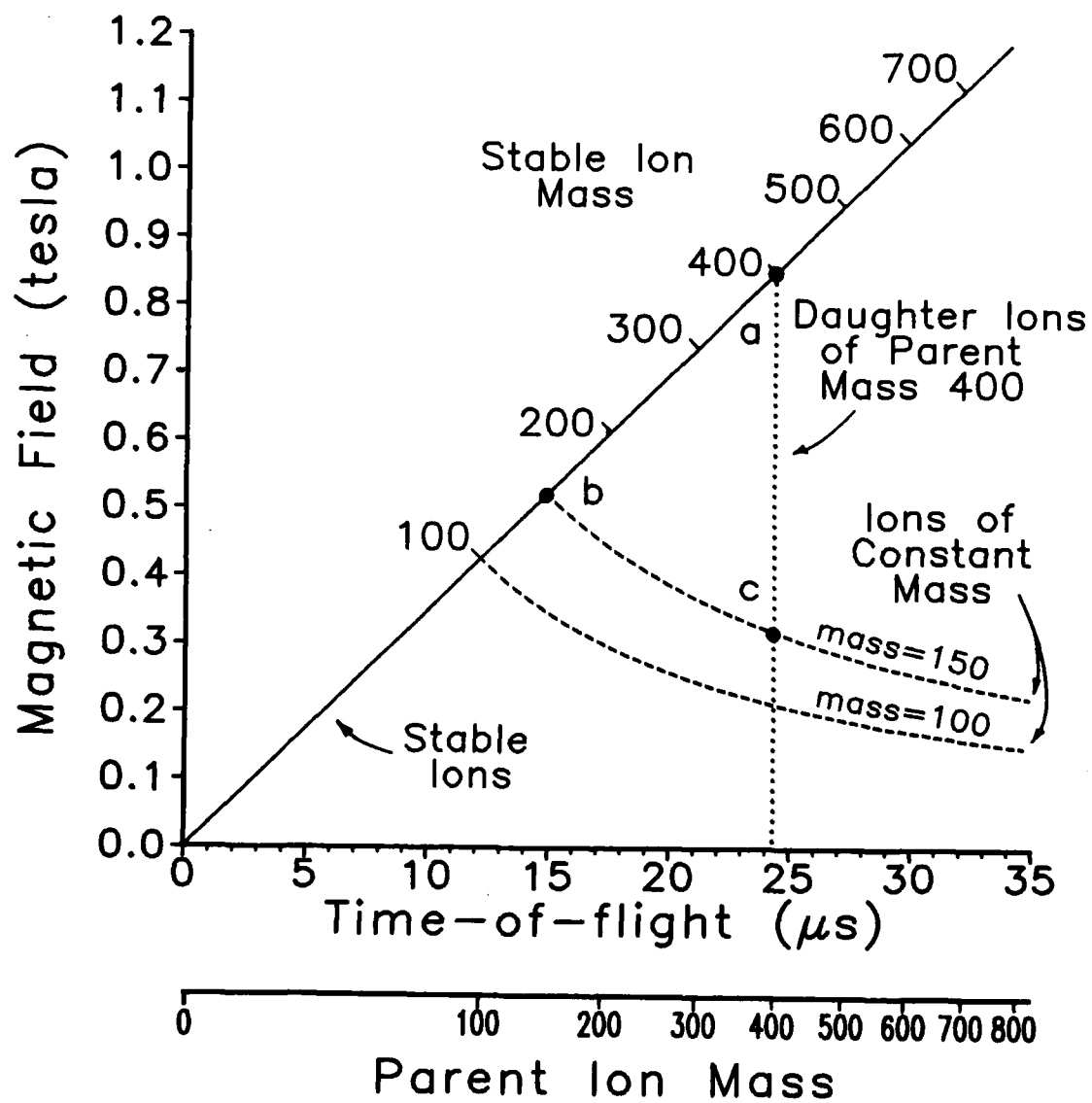
Figure 4 Expanded portion of $\underline{B-t}$ plane illustrating the resolution characteristics. Solid lines represent ion intensity when the uncertainty in the radius and flight length is zero. Shaded portions represent the ion intensity for uncertainties in $\underline{r}$ and $\underline{\ell}$. The uncertainties in the field strength and time define the region of the $\underline{B-t}$ plane sampled.
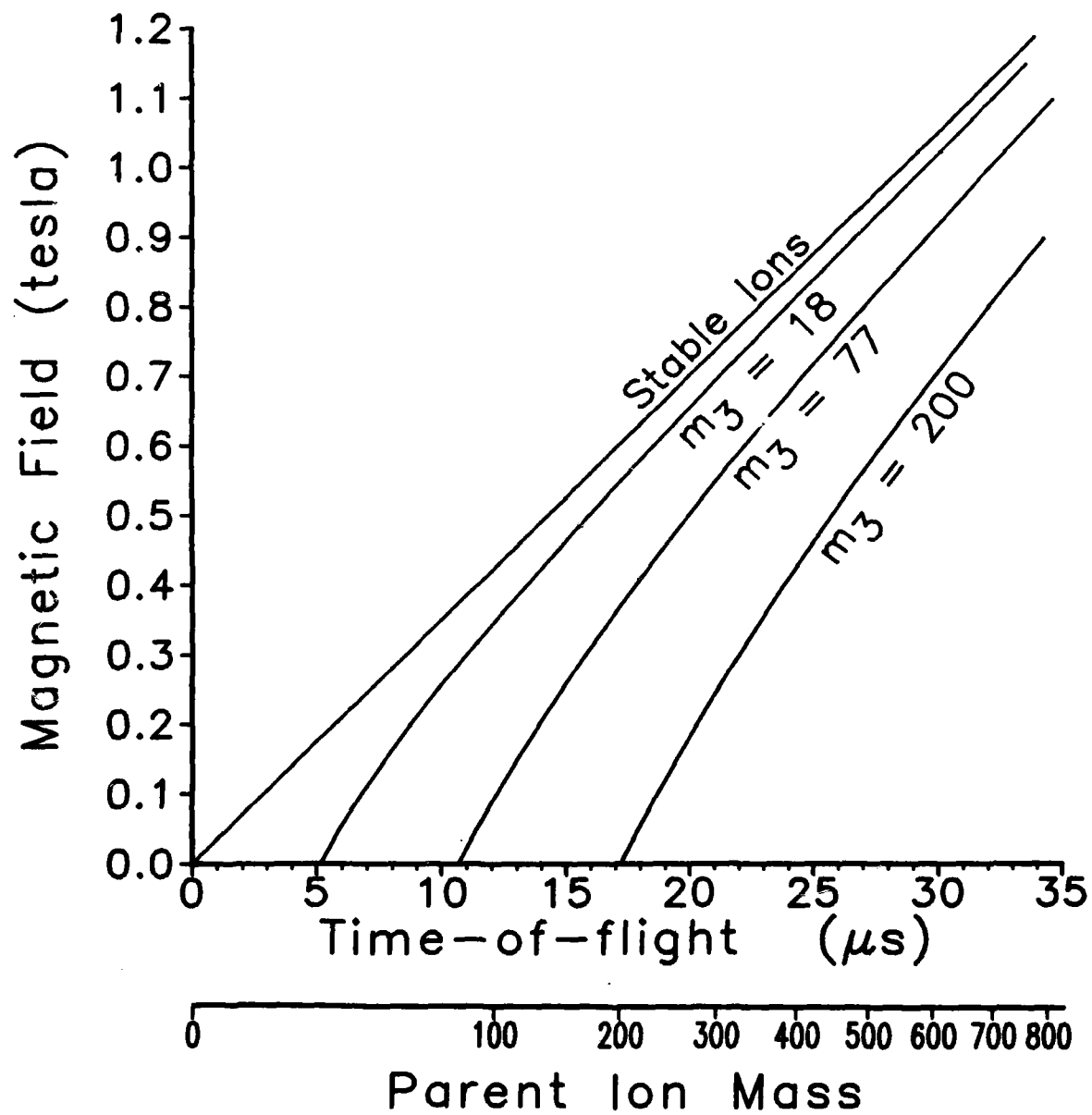
Figure 5 Preliminary data obtained on an LKB-9000 mass spectrometer. A metastable decomposition of benzonitrile yields daughter ions with the same flight time as the parent ion and the same momentum as stable ions of mass 56.
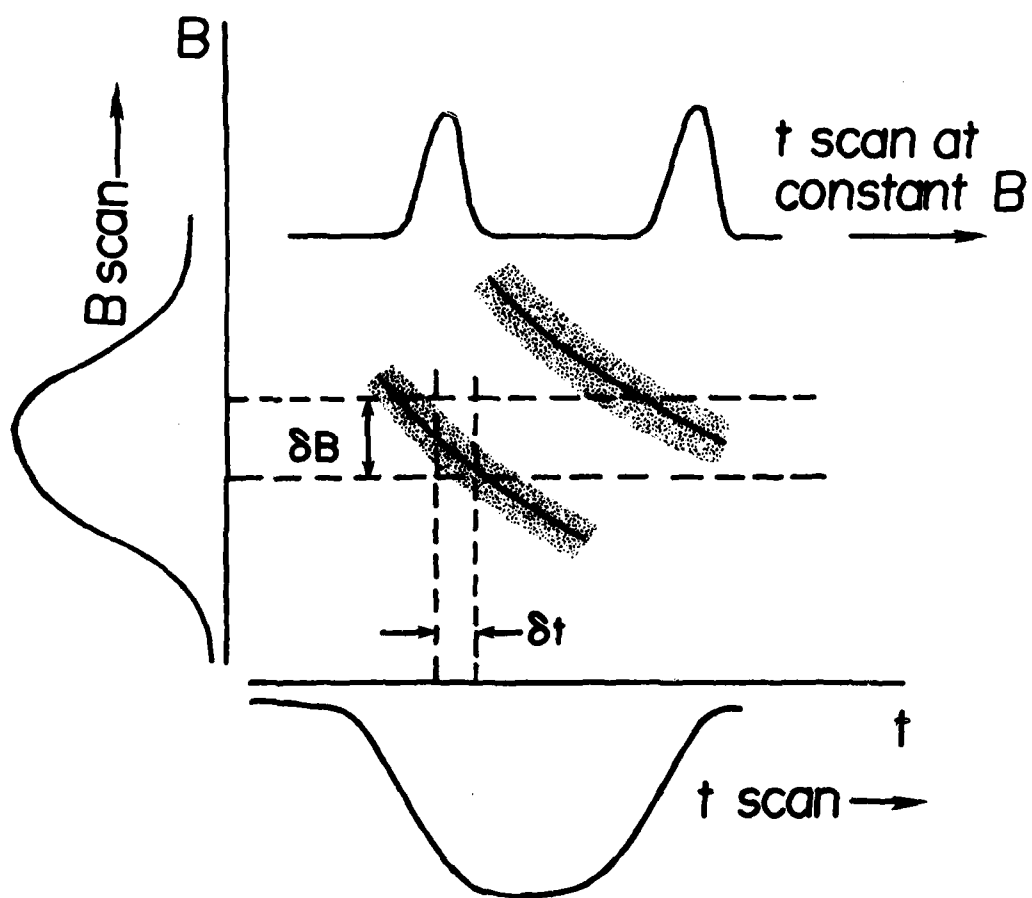
Figure 6 MS/MS data field ($\underline{E}$ $\underline{vs.}$ $\underline{t}$) for the time-resolved ion kinetic energy spectrometer ($\underline{V}$=3500V, $\underline{\ell}$ =1.0m, $\underline{r}$=0.2m). As in Figure 2, each line represents the locus of peaks for a particular type of ion.

Magnetic
Sector

Stable Ions
of Different Mass

Collision
Cell

Daughter Ions of the
Same Parent Ion

Pulsed
Source

Detector

Time →

Magnetic Field (tesla) vs. Time-of-flight (μs) plot showing stable ion mass line, daughter ions of parent mass 400, and ions of constant mass (mass=150, mass=100). Points labeled a, b, c. Lower axis: Parent Ion Mass.

B

B scan →

t scan at
constant B

δB

δt

t

t scan →

BENZONITRILE

$$\underset{p}{103^+} \longrightarrow \underset{d}{76^+} + HCN$$

$$m^* = \frac{d^2}{p} = 56$$

103_s

56_s

TIME (μsec)

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